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(54) DETERGENT COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a Corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent compositions containing cellulose-based soil release ethers. More particularly, the compositions herein are formulated from optimal combinations of anionic and nonionic surfactants which do not substantially interfere with the soil release performance of the cellulose ethers, and which provide superior fabric cleaning performance.

As noted hereinafter, much effort has been expended in designing various compounds which are capable of conferring soil release properties to fabrics during a home laundering operation. The extensive work in this area has, in the main, been directed toward using various polymers as detergent additives with the goal of depositing such polymers onto cotton; polyester and polyester/cotton fabrics from an aqueous laundry bath to secure a soil release benefit in subsequent launderings.

For the most part, the literature relating to soil release polymers indicates that efforts to improve the efficacy of detergent compositions containing such materials as additives has focused on the nature of the polymers themselves and a great variety of such polymers have been prepared and tested.

The continuing search for detergent compositions containing truly effective soil release additives reflects the recognition that many such materials are not particularly useful in this regard, other than at high concentrations. Of course, the use of high concentrations of any additive in detergent compositions is an economic waste if lower amounts would suffice. Moreover, such additives are preferably degraded before being released into water supplies. While many of the prior art soil release materials are entirely acceptable from a toxicological standpoint, their presence in sewage effluents in high concentrations results in an increased biological oxygen demand, with a decrease in water quality. Accordingly, it would be useful to provide detergent compositions containing small, yet effective, amounts of soil release additives.

The most attractive types of soil release polymers are those based on cellulose as a raw material. The cellulose ethers are one such type of polymer. The cellulose ethers are simple to prepare, biodegradable, and are quite acceptable from a toxicological standpoint. Indeed, many such materials are known for use as food additives.

Various cellulose ether soil release polymers are known in the art, and many such materials have been suggested for use both in laundry baths in combination with surfactants and in rinse baths in the absence of surfactants. For example, the use of methyl and ethyl cellulose ethers in detergent compositions is disclosed in U.S. Patent Nos. 2,373,863; 2,994,655; 3,523,088 and British Patent Nos. 1,084,061; 927,542; 765,811 and 340,232, German DAS 1,054,638 and South African Patent No. 71/5129. Clearly, from the standpoint of ease-of-use, it is more convenient to apply the soil release polymers to fabrics in conjunction with a laundering operation and the references reflect the fact that a wide variety of celluloses and mixtures thereof have been suggested for use in detergent compositions. However, the criticality in surfactant selection does not appear to have been appreciated heretofore.

British Patent Application No. 13208/76, (Serial No. 1537287) relates to the discovery that, contrary to the teachings of the prior art, the selection of surfactants for use in combination with cellulose ethers has a substantial and unappreciated effect on their soil release properties. Many detersive surfactants interact with the cellulosics and substantially decrease their efficacy as soil release agents. Accordingly, formulators of detergent compositions containing such materials have been constrained either to accept a sub-optimal level of performance, or to use unduly high concentrations of the cellulose ether polymers in detergent compositions to achieve good soil release performance.

As disclosed in the British Patent application above, certain chain length alkyl sulfate and alkyl benzene sulfonate surfactants are particularly useful for preparing detergent compositions which impart superior soil release properties to fabrics in the presence of but small quantities of cellulose ether soil release agents. Unfortunately, the alkyl sulfate and alkyl benzene sulfonates most compatible with the cellulose soil release ethers are those having relatively short alkyl chains. While optimal from the standpoint of compatibility, these surfactant types do not perform optimally as detergents.

It has now been discovered that certain nonionic surfactants can be used in combination with the longer chain length, more highly detersive anionic surfactants such as the alkyl sulfates and alkyl benzene sulfonates, and these surfactant combinations are compatible with cellulose ether soil release agents. Accordingly, the practice of this invention provides a means for securing the benefits of both the detersive surfactants and the cellulose ethers.

Moreover, it has now been discovered that certain fabric finishes, especially those used on polyester/cotton fabrics, have a substantial effect on the ability of cellulose ethers to provide optimal soil release performance benefits. The soil release ethers used in combination with the preferred surfactant mixtures herein can be selected from a wide range of cellulosics if unfinished polyester/cotton is being laundered. However, if durable-press finished polyesters, or mixed loads are being laundered, it is more preferred to select certain cellulosics which are more robust, i.e., those which perform well on both polyesters and finished and unfinished polyester/cotton blends. The basis for selecting such preferred soil release ethers is disclosed hereinafter.

Various cellulose ethers can be dissolved in distilled water and applied to fabrics especially polyesters, to provide substantial oily soil release benefits. For the most, part, when such ethers are formulated in detergent compositions containing surfactants and builders, the soil release performance of the ethers decreases markedly. It has now been found that the problem of the decrease in the inherently good oily soil release performance of cellulose ethers can be overcome without sacrificing overall detergency performance on other types of soil.

The present invention is based on the discovery that anionic surfactants such as the long chain alkyl sulfates and long chain alkyl benzene sulfonates can be combined with certain nonionic surfactants to provide highly detersive mixtures which have much less of an inhibitory effect on the soil release performance of cellulose-based ethers than do long chain anionics used separately. Accordingly, by proper selection of anionic/nonionic surfactant mixtures, it is now possible to provide detergent compositions having both excellent fabric cleaning properties and through-the-wash soil release properties, while using substantially less cellulose soil release material than was heretofore thought possible.

Moreover, it has now been discovered that fabric finishes commonly used on polyester/cotton fabrics can substantially affect the soil release performance properties of cellulose soil release ethers. Accordingly, when formulating optimal compositions in the manner of this invention, it is highly preferred to select both a preferred anionic/nonionic surfactant mixture and a preferred cellulosic, all as described more fully hereinafter.

Finally, it has been discovered that the removal of electrolytes (e.g., water-soluble builders) can further enhance the soil release performance of the surfactant/cellulose ether compositions herein. Highly preferred, zeolite-built detergent compositions substantially free from water-soluble builders are described hereinafter.

The present invention encompasses detergent compositions, comprising:

(a) from 5% to 65% by weight of a mixed surfactant component comprising a water-soluble anionic surfactant which is an alkyl sulfate, alkyl ether sulfate, alkyl sulfonate, alkyl ether sulfonate or alkyl benzene sulfonate, or a mixture thereof, wherein the term alkyl includes alkenyl groups, said alkyl groups having 8 to 22 carbon atoms, and a water-soluble nonionic surfactant, or a mixture thereof, selected from the group

consisting of primary C_{10} to C_{20} alcohol ethoxylates containing 9 to 30 ethoxyl groups, secondary C_{10} to C_{20} alcohol ethoxylates containing 9 to 30 ethoxyl groups, and (C_8 to C_{12} alkyl) phenol ethoxylates containing 9 to 30 ethoxyl groups, said nonionic surfactant being characterized by an EO: hydrocarbon ratio of from 0.6:1 to 3:1, at a weight ratio of anionic: nonionic from 15:1 to 1:1 (most preferably 3:1);

(b) from 0.1% to 3% by weight of a soil release ether component selected from the group consisting of alkyl cellulose ethers, hydroxyalkyl cellulose ethers and hydroxyalkyl alkyl cellulose ethers;

(c) from 0% to 70% by weight of a detergency builder component; and

(d) the balance of the composition comprising detergency adjunct materials and carriers.

Preferred compositions herein are characterized by a weight ratio of anionic surfactant: soil release ether of from 5:1 to 100:1, most preferably 10:1 to 30:1.

The *detergent compositions* of the present invention comprise two essential components, the mixed anionic/nonionic surfactant component and the cellulose ether soil release component, as described more fully hereinafter.

Anionic Surfactant Component

It will be recognized that the anionic surfactants used herein are the typical alkyl benzene sulfates and sulfonates, alkyl sulfates and sulfonates, and ethoxylated alkyl ether sulfates and sulfonates well-known in the detergency arts. Such anionic surfactants are readily available from a variety of well-known commercial processes and sources.

More particularly, the anionic surfactants employed herein are any of the water-soluble detersive materials of the type disclosed above. Mixtures of the foregoing anionic surfactants can also be employed herein. The preferred anionic surfactants herein include the C_{10}—C_{18} alkyl benzene sulfates; C_{10}—C_{18} alkyl benzene sulfonates; C_{10}—C_{18} alkyl sulfates; C_{10}—C_{18} alkyl sulfonates; ethoxylated C_{10}—C_{18} alkyl ether sulfates; and ethoxylated C_{10}—C_{18} alkyl ether sulfonates.

Highly preferred anionic surfactants employed herein by virtue of their superior detergency performance are the C_{12}—C_{16} alkyl benzene sulfonates; the C_{14}—C_{18} alkyl sulfates and the C_{12}—C_{18} ethoxylated alkyl ether sulfates.

The anionic surfactants herein can be employed in their free acid form. However, inasmuch as detergency performance in an aqueous liquor is usually substantially higher at basic pH's, the surfactants herein are generally used in the form of their water-soluble salts. As noted hereinabove, any counterion which provides a water-soluble salt of the anionic surfactant is suitable for use, but the surfactants are most commonly and preferably used in their sodium salt form, for reasons of economy.

The following is a listing of anionic surfactants which are representative of those employed in the present invention, but is not intended to be limiting thereof.

The alkyl benzene sulfate and sulfonate surfactants employed herein can be, for example, sodium dodecylbenzene sulfate; potassium dodecylbenzene sulfonate; sodium tetradecylbenzene sulfate; triethanolammonium tetradecylbenzene sulfonate; ammonium hexadecylbenzene sulfate; ammonium hexadecylbenzene sulfonate; diethanolammonium octadecylbenzene sulfonate; and monoethanolammonium octadecylbenzene sulfonate. In the alkyl benzene-based anionic surfactants, the alkyl group can either be in straight chain or branched chain configuration; the straight chain configuration is preferred, inasmuch as these compounds are biodegradable.

It will be recognized that, on a commercial scale, the alkyl benzene sulfates and sulfonates are readily prepared from petroleum fractions comprising mixtures of alkyl benzene feedstocks containing various chain length alkyl substituents. Alkyl benzene sulfates and sulfonates prepared from such mixed feedstocks are entirely suitable for use herein, and are preferred for economic reasons. The most highly preferred mixtures of the alkyl benzene-based anionic surfactants herein are those containing major proportions of the "heavy" or long-chain alkyl materials. An especially preferred anionic mixture herein comprises the alkyl benzene sulfonates containing an average of about 11.8 carbon atoms in linear configuration in the alkyl group (abbreviated $C_{11.8}$ LAS).

The alkyl sulfate surfactants employed herein are materials which are available from petrochemical and alcohol-based feedstocks. Specific examples of the alkyl sulfates and sulfonates useful herein include decyl sulfate; decyl sulfonate; dodecyl sulfate; dodecyl sulfonate; tetradecyl sulfate; tetradecyl sulfonate; hexadecyl sulfate; hexadecyl sulfonate; octadecyl sulfate; and octadecyl sulfonate. The most highly preferred alkyl sulfates and alkyl sulfonates herein are those wherein the alkyl chain length is from about C_{14} to about C_{16}.

As in the case of the alkyl benzene-based anionic surfactants, the alkyl sulfates and sulfonates herein are most commonly employed in the form of water-soluble salts, with the sodium salt being the most preferred. Specific examples of preferred alkyl sulfates and sulfonates herein include sodium tetradecyl sulfate; ammonium tetradecyl sulfate; sodium hexadecyl sulfate; triethanolammonium hexadecyl sulfonate; monoethanolammonium octadecyl sulfate; triethanolammonium octadecyl sulfate; and sodium octadecyl sulfate.

As with the alkyl benzene-based anionic surfactants, mixtures of the alkyl sulfates and sulfonates can also be employed herein. Again, it is preferred that such mixtures contain major proportions of the long-chain, i.e., C_{14} and greater, alkyl substituents, inasmuch as such compounds are better detergents than their shorter-chain homologs.

Mixed alkyl sulfates, especially those which can be prepared from the mixed fatty alcohols commonly known as coconut fatty alcohols and tallow fatty alcohols, are especially preferred herein for economic reasons. A highly preferred alkyl sulfate mixture herein comprises the so-called tallow alkyl sulfates, and these contain more of the longer-chain alkyl materials than does the coconut-range fraction.

A third type of anionic surfactant useful in the present invention encompasses the ethoxylated alkyl ether sulfates and sulfonates. Typically, such materials comprise a C_{10}—C_{18} alkyl group which is ethoxylated with from 1 to about 20, more preferably 3 to about 10, ethoxyl groups, which are subsequently sulfated or sulfonated at the terminal position of the molecule. As with the alkyl sulfates, such ethoxylated materials can be mixtures resulting from the use of mixed alkyl feedstocks such as the coconut alcohols or tallow-based alcohols.

The ethoxylated alkyl ether anionic surfactants herein are typically employed in their salt form, with the sodium salt being preferred for economic reasons.

Representative, non-limiting examples of the ethoxylated alkyl ether surfactants employed herein are as follows. Following common practice, the degree of ethoxylation (EO) is indicated by the subscript notation. It is to be recognized that, in commercial practice, the degree of ethoxylation is commonly represented as an average of a given ethoxylated mixture. Sodium dodecyl $(EO)_3$ sulfate; potassium hexadecyl $(EO)_6$ sulfate; triethanolammonium octadecyl $(EO)_9$ sulfate; sodium decyl $(EO)_3$ sulfonate; and diethanolammonium octadecyl $(EO)_{12}$ sulfonate are all useful as the anionic surfactant of the present invention.

Mixed ethoxylated alkyl sulfates, such as sodium coconutalkyl $(EO)_6$ sulfate and sodium tallowalkyl $(EO)_6$ sulfate, are particularly useful herein, inasmuch as these materials are commercially available and contain substantial portions of the higher (C_{14} and greater) optimally detersive alkyl ether sulfates.

Nonionic Surfactant Component

The instant detergent compositions employ a nonionic surfactant which serves to compatibilize the anionic surfactant and the cellulose soil release ether. The nonionic surfactants herein are used at a weight ratio of anionic: nonionic of from 15:1 to 1:1, more preferably from about 4:1 to about 1.5:1, to achieve this compatibilizing function. While not intending to be limited by theory, it is hypothesized that the mixed anionic/nonionic micellar surfactant structures which are formed in an aqueous laundering bath containing the instant detergent compositions do not undesirably interact with cellulose ethers in the manner of the "free" anionic surfactant monomers.

The nonionic surfactants employed herein are specified condensation products of relatively long chain ethylene oxide moieties with primary alcohols, secondary alcohols, or alkyl phenols. Such nonionic surfactants are well-known in the detergency art. However, the gist of the present invention is the discovery that the aforesaid ethylene oxide-based nonionic surfactants which are rendered substantially free from the shorter-chain ethylene oxide condensates and free alcohols commonly present in commercial mixtures of such materials serve to compatibilize the anionic surfactant with the cellulose ethers herein.

More specifically, nonionic surfactants of the formula $R''(EO)_x$, wherein: R'' is a straight- or branched-chain hydrocarbyl moiety derived from a primary or secondary alcohol containing from about 8 to about 20, more preferably from about 10 to about 18, carbon atoms, or an alkyl phenol-based moiety wherein the alkyl chain is straight or branched and contains from 6 to 12 carbon atoms; EO is the standard abbreviation for the ethylene oxide moiety; and wherein subscript x denotes the degree of polymerization of the ethylene oxide moiety and is an integer of at least about 9, preferably the ratio of x to the number of carbon atoms in the hydrocarbyl moiety, i.e., the EO:hydrocarbon ratio, is from 0.6:1 to 3:1, comprise the compatibilizing

surfactants herein. The associated abbreviation C_n, wherein subscript n is an integer, hereinafter denotes an alkanol with n carbon atoms (the prefixes n- and sec- denoting any chain branching in the usual way).

It has been discovered that the more highly water-soluble nonionics, especially the C_{10}—C_{16} (EO)$_y$ to (EO)$_{24}$ compounds, are particularly suitable for compatibilizing the anionic surfactants so that they can be used in combination with the cellulose ethers. More specifically, ethoxylated nonionic surfactants of the type

$$R''(OCH_2CH_2)_{x-2}OCH_2CH_2OH$$

wherein R'' is alkyl or alkenyl or alkyl benzene and x is an integer, all as defined above, are useful herein as the compatibilizing surfactant. Specific, non-limiting examples of such nonionic surfactants include the following: n-C_{10}(EO)$_9$, n-C_{12}(EO)$_{12}$, n-C_{14}(EO)$_{13}$, n-C_{10}(EO)$_{15}$, n-C_{12}(EO)$_{24}$, n-C_{12}(EO)$_{30}$, sec-C_{10}(EO)$_8$, sec-C_{12}(EO)$_{12}$, sec-C_{14}(EO)$_{20}$, sec-C_{16}(EO)$_{30}$, decyl benzene (EO)$_{12}$, dodecyl benzene (EO)$_{15}$ and tetradecyl benzene (EO)$_{20}$.

The foregoing pure nonionic surfactants, and mixtures thereof, are all useful herein. However, it will be recognized that such pure materials are relatively expensive to prepare, in that they involve separation of pure alcohol or alkyl benzene phenol precursors, followed by ethoxylation and a second separation procedure to secure the pure compounds. For economic reasons, therefore, it is more preferred to use mixtures of such materials, and such mixtures are suitable for use herein when "stripped" of substantially all of the lower ethoxylates and unreacted alcohol or alkyl phenol precursors commonly present in such mixtures. For example, mixtures of alcohols such as the tallow alcohols or coconut alcohols can be ethoxylated to an average degree of about 9—12. The resulting product will contain some of the shorter-chain ethoxylates, such as the triethoxylate, hexa-ethoxylate, and the like, as well as some unreacted alcohol. These shorter-chain materials are more volatile than the desired longer-chain ethoxylates and can be substantially removed from the reaction mixture by distillation or other well-known separation techniques. The resulting "stripped" nonionic mixture is thereby enriched in the desirable longer-chain ethoxylates and is preferred for use herein.

As can be seen from the foregoing, a variety of ethoxylated materials, even those having a degree of ethoxylation of up to 30, and higher, are useful as the compatibilizing nonionic surfactant in the manner of the present invention. It will be recognized that it is highly desirable that all surfactant components present in a finished detergent formulation contribute to the detergency power thereof. Moreover, it is well-known that certain ethoxylated nonionic surfactants are particularly useful for removing oily soils from synthetic fabrics such as polyesters, whereas other nonionic surfactants are not. For this reason, it is highly preferred herein to select nonionic surfactants which not only compatibilize the anionic surfactant with the soil release ether, but also contribute in a significant way to the overall detergency performance of the finished composition. In general terms, the C_{10}—C_{13} (EO)$_y$ to (EO)$_{12}$ ethoxylates are preferred herein, inasmuch as they are both useful compatibilizing agents and detersive surfactants.

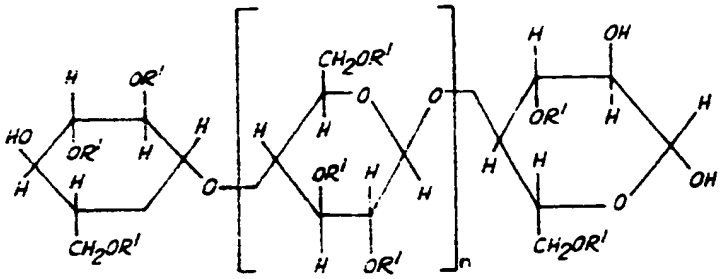
More particularly, the preferred, detersive compatibilizing surfactants herein comprise the condensation product of polyethylene oxide containing from about 9 to about 12 ethylene oxide moieties with primary and secondary C_{10} to C_{14} alcohols and alkyl phenols wherein the alkyl substituent contains from about 6 to about 9 carbon atoms. The alcohol ethoxylates are more preferred herein than the alkyl phenol ethoxylates, from the standpoint of cost and biodegradability.

Specific, but not limiting, examples of such preferred, detersive compatibilizing nonionic surfactants herein include: n-C_{10}(EO)$_5$; "stripped" C_{9-10} alcohol (EO)$_5$ as "Dobanol" (a Trade Mark) 91—8 Shell; "Dobanol" 91—12; and Neodol 01 E_{12} (C_{10-11} alcohol avg. 12 EO groups, Shell).

Soil Release Ether Component

The soil release component herein comprises etherified cellulose. The basic structure of the cellulose ethers used in the present compositions can be depicted as follows, wherein n is an integer in the range of from about 100 to about 10,000, and wherein R' represents alkyl, hydroxyalkyl, or mixed alkyl and hydroxyalkyl substituents, as described herein after and having a DS alkyl theoretical maximum value as described hereinafter. Useful alkyl groups include methyl, ethyl, propyl, butyl, pentyl, isobutyl, hexyl and nonyl. Preferred alkyl groups include methyl, ethyl, propyl and butyl, with methyl being most preferred from the standpoint of cost, ease of

manufacture and performance. Preferred hydroxyalkyl groups include hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl, with hydroxybutyl being most preferred. Highly preferred, commercially available materials have R' as mixtures of methyl and hydroxybutyl.



Processes for preparing the cellulose ethers are known and form no part of this invention. Briefly, when preparing the alkyl cellulose ether soil release agents employed in the present compositions, the hydroxyl groups of the anhydroglucose units of cellulose are reacted with an alkylating agent, thereby replacing the hydrogen of the hydroxyls with alkyl substituents. The number of substituent alkyl groups can be designated by weight percent, or by the average number of alkyl (i.e., as alkoxyl) groups on the anhydroglucose units, i.e., the Degree of Substitution (DS) alkyl. If all three available positions on each anhydroglucose unit are subsituted, the DS alkyl is designated three (3); if an average of two —OH's are substituted, the DS alkyl is designated two (2), etc. Similar nomenclature is used to define the hydroxyalkyl and hydroxyalkyl alkyl cellulose ethers employed herein. When describing the hydroxyalkyl alkyl cellulosics, the degree of substitution of both substituent types is set forth.

Commercial processes for preparing alkyl cellulose ethers involve, for example, simply combining the desired alkyl halide, e.g., methyl chloride, with a cellulose feed stock of the type disclosed hereinafter under alkaline conditions. (It is to be understood that the alkyl halides used to prepare the cellulose soil release agents herein can contain minor amounts of alkyl halides other than that selected. The resulting cellulose ethers may contain very minor proportions of mixed alkyl groups. This is not important to the invention herein.) Such a process results in a DS alkyl below 2, and most generally a DS alkyl of about 1.5.

Higher DS alkyl cellulose ethers can be prepared by the exhaustive alkylation of cellulose using an alkyl halide, e.g., methyl chloride, and caustic, preferably sodium hydroxide, in a pressure vessel in the manner well known in the art for preparing the lower DS alkyl cellulosics. However, the alkylation procedure can simply be repeated and continued until the higher DS materials are secured. In either case, the progress of the alkylation reaction can be monitored by periodically sampling the reaction product and determining the degree of alkoxylation by various means well known in the art.

The exhaustive alkylation procedure herein results in the formation of cellulose ethers having a DS alkyl in the range of about 1.7 to about 3.0 (theoretical maximum). One class of highly preferred alkyl cellulose ethers herein has group R' as methyl and is characterized by a DS methyl in the range of about 2.0 to about 2.7.

The manufacture of the hydroxyalkyl alkyl cellulose soil release agents used herein is also carried out using well-known procedures. In a typical method, a cellulose feedstock is swelled with caustic soda solution to produce alkali cellulose, which is then treated with an alkyl halide (preferably methyl chloride) and an alkylene oxide (preferably butylene oxide). The DS alkyl and DS hydroxyalkyl of the resulting cellulose ether can be varied, depending on the reaction stoichiometry and reaction times and temperatures used, all in well-known fashion.

Similarly, hydroxyalkyl cellulose ethers can be prepared by reacting cellulose feedstocks with an alkylene oxide and caustic, usually at elevated temperatures and pressures, in the manner known in the art.

The cellulose feedstocks used to prepare the soil release ethers herein can be, for example, wood pulp or cotton linters. The harsh alkaline conditions of the etherification reaction commonly reduce the degree of polymerization (integer n in the foregoing formula) to 100—2000. This is of no substantial consequence to the present invention.

Representative, non-limiting examples of cellulose soil release agents used herein

are as follows: methyl cellulose DS methyl 1.5; ethyl cellulose DS ethyl 1.2; methyl ethyl cellulose DS methyl 1.0, DS ethyl 0.7; hydroxyethyl cellulose cellulose DS hydroxyethyl 1.2; hydroxypropyl cellulose DS hydroxypropyl 1.5; methyl hydroxyethyl cellulose DS methyl 1.5, DS hydroxyethyl 0.1; methyl hydroxyethyl cellulose DS methyl 1.5, DS hydroxyethyl 0.5; and butyl cellulose DS butyl 1.5.

The cellulose ethers employed herein are water-soluble and are characterized by a negative temperature coefficient of solubility. Being polymeric, and having the potential for inter-molecular association by virtue of their side-chain substituents, the cellulose ethers herein increase the viscosity of aqueous solutions, especially when present therein in concentrations of about 2%. The solution viscosity of the cellulose ethers is unimportant when preparing granular detergent compositions, inasmuch as they are ultimately present in the aqueous laundry bath in such small concentrations. However, when preparing liquid detergent compositions in the manner of the present invention the solution concentration of the soil release ether is high enough that viscosity can be a problem. For example, it is desirable to provide liquid detergent compositions which are readily pourable and measurable, and which are not of a gelatinous or syrupy consistency. When preparing such liquid detergent compositions, it is preferred to select a cellulose ether of the foregoing type having a solution viscosity below about 250 centipoise (cps). Preferably, the solution viscosity of the cellulose ethers employed in the liquid detergent compositions prepared according to the present invention lies in the range from about 20 cps to about 200 cps (measured as a 2% wt. aqueous solution at 32°C).

It is to be understood that by selecting the narrow cut of surfactants as disclosed herein the soil release efficacy of detergent compositions containing substantially all soil release ethers of the type disclosed above is optimized in the general manner disclosed in the Figure. That is to say, the select surfactants employed herein interfere much less with the inherent soil release properties of the cellulose ethers (as measured by deposition on fabrics from pure distilled water) than do other members of the surfactant class falling outside the recited range. However, this is not to say that all soil release ethers are equivalent in their soil release performance on fabrics, especially polyester and polyester/cotton blends. Certain cellulose ethers inherently provide less of a soil release benefit than do others, even when applied to fabrics from distilled water in the absence of interfering surfactants. For example, certain hydroxypropyl cellulosics are inherently poorer in their soil release performance, even when applied to fabrics from an aqueous medium in the absence of any surfactants, than the methyl hydroxybutyl cellulosics applied in similar fashion. This difference in performance naturally carries over to compositions containing the surfactants disclosed herein. Accordingly, to provide optimal soil release performance it is preferred to choose certain of the herein-disclosed soil release ethers for use in combination with the disclosed select group of surfactants.

Moreover, it has now been found that, while the soil release performance of any of the cellulosics is better when used in combination with the preferred surfactants disclosed herein than with those falling outside the class, performance is detrimentally affected by fabric finishes. However, it has been discovered that certain cellulosics function well, even on finished polyester/cotton fabrics. Accordingly, it is now possible to describe highly preferred, robust cellulose ethers which are suitable for use in combination with the select group of surfactants to impart soil release properties to both polyester and finished and unfinished blend fabrics.

Preferred alkyl cellulose ethers herein are the C_1 to C_4 alkyl ethers, especially methyl, having a DS alkyl of from 1.0 to about 3.0. Alkyl ethers having a DS alkyl of from about 1.3 to about 2.0 are commercially available and are especially useful members of this class of soil release ethers.

Preferred hydroxyalkyl cellulose ethers herein are the hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl cellulosics having a DS hydroxyalkyl of from 1.2 to 2.9, more preferably 1.3 to 1.7. As a class, the hydroxyalkyl cellulosics are somewhat lower in soil release performance than the alkyl or mixed hydroxyalkyl alkyl cellulosics. Nevertheless, these materials are useful herein and offer the advantage of somewhat higher water solubility than the other classes of cellulosics, with attendant advantages in liquid formulations.

The hydroxyalkyl alkyl cellulosics, especially those having a DS hydroxyalkyl of at least about 0.01 and a DS alkyl of at least about 1.0, preferably a DS alkyl from 1.3 to 2.5, form an especially preferred class of soil release ethers herein from the standpoint of their inherently good soil release performance. Many such materials are commercially available.

Preferred hydroxyalkyl alkyl cellulosics are those wherein the DS hydroxyalkyl is

at least 0.05, the DS alkyl is at least 1.0 and the total DS (alkyl+hydroxyalkyl) is at least 1.05, more preferably at least 1.5. Hydroxyalkyl alkyl cellulosics wherein the alkyl group is C_1—C_4, especially methyl, and wherein the hydroxyalkyl group is hydroxymethyl hydroxyethyl, hydroxypropyl or hydroxybutyl, are especially preferred.

When preparing robust detergent compositions suitable for use on either finished or unfinished fabrics, especially polyester/cottons, it is preferable to select cellulose ether from either the alkyl or hydroxyalkyl alkyl classes set forth above. The most robust alkyl cellulose ethers are those having a relatively high DS alkyl, in the range of 1.7 to 2.7. These high DS alkyl cellulosics are readily prepared by the exhaustive alkylation procedure set forth above. Methyl cellulose ethers characterized by a DS methyl in the range of 1.8 to 2.2 are readily available and especially preferred in the present compositions.

Robust hydroxyalkyl alkyl cellulosics also fall within the more highly substituted members of this class, especially with regard to their DS alkyl. Preferred among this class are those cellulosics having a DS alkyl in the range of 1.7 to 2.7, especially 1.8 to 2.2, with methyl being the preferred alkyl substituent. The DS hydroxyalkyl in this preferred class of cellulosics is less critical than the DS alkyl, and falls within a range of 0.01 to 1.0, most preferably 0.06 to 1.0. Hydroxybutyl is the most preferred hydroxyalkyl substituent.

Especially preferred herein is methyl hydroxybutyl cellulose, DS methyl avg. 1.8—2.2, DS hydroxybutyl avg. 0.08, available under the Trademark "Methocel" HB. Other preferred ethers include ethyl hydroxyethyl cellulose DS ethyl 1.7, DS hydroxyethyl 0.9; and methyl hydroxyethyl cellulose DS methyl 1.7, DS hydroxyethyl 0.09.

As disclosed hereinabove the solution viscosity of the cellulose ethers is not critical to their performance. However, this parameter, used in combination with the DS alkyl and DS hydroxyalkyl, does help further specify the highly preferred, robust cellulosics herein. The solution viscosity (2% aqueous) of these cellulosics lies in the wide range of about 100 cps to 25000 cps, more particularly 400 cps to 15000 cps.

It is to be understood that the common anionically substituted cellulosics, e.g., carboxymethyl cellulose, do not fall within the definition of cellulose ethers herein. Such anionic cellulosics are not contemplated for use as the soil release ether component herein, but can be present in minor quantities in the instant compositions for their known performance benefits as soil suspending agents, carriers and thickeners.

Detergency Builders and Adjuncts

The instant compositions can optionally contain all manner of detergency builders commonly taught for use in detergent compositions. The detergent compositions herein can contain from 0% to 70% by weight, preferably from 15% to 65% by weight, of said builders. Useful builders herein include any of the conventional inorganic and organic water-soluble builder salts, as well as various water-insoluble and so-called "seeded" builders.

Inorganic detergency builders useful herein include, for example, water-soluble phosphates, pyrophosphates, orthophosphates, polyphosphates, polyphosphonates, carbonates, polyhydroxysulfonates, silicates, polyacetates, carboxylates, polycarboxylates and succinates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates, and hexametaphosphates. The polyphosphonates specifically include, for example, the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Examples of these and other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148. Sodium tripolyphosphate is an especially preferred, water-soluble inorganic builder herein.

Non-phosphorus containing sequestrants can also be selected for use herein as detergency builder.

Specific examples of non-phosphorus, inorganic builder ingredients include water-soluble inorganic carbonate, bicarbonate, and silicate salts. The alkali metal, e.g., sodium and potassium, carbonates, bicarbonates, and silicates are particularly useful herein.

Water-soluble, organic builders are also useful herein. For example, the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulfonates are useful builders in the present compositions and processes. Specific examples of the polyacetate and polycarboxylate builder salts include sodium, potassium, lithium, ammonium and substituted ammonium salts of

ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, other benzene polycarboxylic acids, and citric acid.

Highly preferred non-phosphorus builder materials (both organic and inorganic) herein include sodium carbonate, sodium bicarbonate, sodium silicate, sodium citrate, sodium oxydisuccinate, sodium mellitate, sodium nitrilotriacetate, and sodium ethylenediaminetetraacetate, and mixtures thereof.

Other highly preferred organic builders herein are the polycarboxylate builders set forth in U.S. Patent 3,308,067, Dichl.

Examples of such materials include the water-soluble salts of homo- and co-polymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalonic acid.

Additional, preferred builders herein include the water-soluble salts, especially the sodium and potassium salts, of carboxymethyloxymalonic, carboxymethyloxysuccinic, cis-cyclohexanehexacarboxylic, cis-cyclopentanetetracarboxylic and phloroglucinol trisulfonic acids.

Sodium nitrilotriacetate is an especially preferred, water-soluble organic builder herein.

Another type of detergency builder material useful in the present compositions and processes comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations in combination with a crystallization seed which is capable of providing growth sites for said reaction product. "Seeded builder" compositions are disclosed in British Patent Specification No. 1,424,406.

More particularly, the seeded builders useful herein comprise a crystallization seed having a maximum particle dimension of less than 20 microns, preferably a particle diameter of from about 0.01 micron to about 5 microns, in combination with a material capable of forming a water-insoluble reaction product with free metal ions.

Many builder materials, e.g., the water-soluble carbonate salts, precipitate water hardness cations, thereby performing a builder function. Unfortunately, many of the precipitating builders used in detergent compositions do not reduce the free metal ion content of laundry baths quickly, and such builders only compete with the organic detergent and the soil for the free metal ions. The result is that while some of the free metal ions are removed from the solution, some ions do react with the organic detergent and the soil, thereby decreasing the detersive action. The use of the crystallization seed quickens the rate of precipitation of the metal hardness, thereby removing the hardness ions before they can adversely affect the detergency performance.

By using a material capable of forming a water-insoluble product with free metal ions in combination with a crystallization seed, the combined free metal ion concentration of an aqueous laundering liquor can be reduced to less than 0.5 grains of hardness within about 120 seconds. In fact, the preferred seeded builders can reduce the free metal hardness to less than 0.1 grains/gallon within about 30 seconds.

Preferred seeded builders consist of: a water-soluble material capable of forming a reaction product having a solubility in water of less than about 1.4×10^{-2} wt.% (at 25°C with divalent and polyvalent metal ions such as calcium, magnesium and iron; and a crystallization seed (0.001—20 micron diameter) which comprises a material which will not completely dissolve in water within 120 seconds at 25°C.

Specific examples of materials capable of forming the water-insoluble reaction product include the water-soluble carbonates, bicarbonates, sesquicarbonates, silicates, aluminates and oxalates. The alkali metal, especially sodium, salts are preferred for convenience and economy.

The crystallization seed employed in such seeded builders is preferably selected from the group consisting of calcium carbonate; calcium and magnesium oxalates; barium sulfate; calcium, magnesium and aluminum silicates; calcium and magnesium oxides; calcium and magnesium salts of fatty acids having 12 to 22 carbon atoms; calcium and magnesium hydroxides; calcium fluoride; and barium carbonate. Specific examples of such seeded builder mixtures comprise: 3:1 wt. mixtures of sodium carbonate and calcium carbonate having a 5 micron particle diameter; 2.7:1 wt. mixtures of sodium sesquicarbonate and calcium carbonate having a particle diameter of 0.5 microns; 20:1 wt. mixtures of sodium sesquicarbonate and calcium hydroxide having a particle diameter of 0.01 micron; and a 3:3:1 wt. mixture of sodium carbonate, sodium aluminate and calcium oxide having a particle diameter of 5 microns.

A seeded builder comprising a mixture of sodium carbonate and calcium carbonate

is especially preferred herein. A highly preferred seeded builder comprises a 30:1 to 5:1 (wt. Na_2CO_3:$CaCO_3$) mixture of sodium carbonate and calcium carbonate wherein the calcium carbonate has an average particle diameter from 0.01 micron to 5 microns.

Another type of builder useful herein includes various substantially water-insoluble materials which are capable of reducing the hardness content of laundering liquors, e.g., by ion-exchange processes. Examples of such builder materials include the phosphorylated cloths disclosed in U.S. Patent 3,424,545, to R. A. Bauman, issued January 28, 1969.

As noted above, the avoidance of electrolytes (e.g., water-soluble builder salts) has an additional positive effect on the soil release performance of the cellulose ether/surfactant compositions herein. Therefore, it is particularly advantageous to provide compositions comprising the preferred surfactant, cellulose ether, and a non-electrolyte (i.e., water-insoluble) builder material.

The complex aluminosilicates, i.e., zeolite-type materials, are especially useful builders in the present compositions, since these materials are water-insoluble and readily soften water, i.e., remove Ca^{++} hardness. Both the naturally occurring and synthetic "zeolites", especially the zeolite A and hydrated zeolite A materials, are useful for this builder/softener purpose, and do not interfere with the cellulose ethers. A description of zeolite A materials and a method of preparation appears in U.S. Patent 2,882,243, entitled Molecular Sieve Adsorbents, issued April 14, 1959.

The compositions herein can contain all manner of detergent adjunct materials and carriers commonly found in laundering and cleaning compositions. For example, various perfumes, optical bleaches, fillers, anti-caking agents and fabric softeners can be present to provide the usual benefits occasioned by the use of such materials in detergent compositions.

Perborate bleaches commonly employed in European detergent compositions can also be present as a component of the instant detergent compositions, and are added thereto as dry admixes.

Enzymes, especially the thermally stable proteolytic and lipolytic enzymes used in laundry detergents, can be dry-mixed in the compositions herein.

Materials such as sodium sulfate can be used as fillers for the granular compositions herein. Water and water-alcohol mixtures (especially 20:1 to 10:1 wt. water/ethanol mixtures) are useful carriers for liquid compositions comprising the surfactant and soil release ethers disclosed herein.

Product Testing

The soil release efficacy of the compositions herein is tested using a typical, hard to remove, greasy soil, dirty motor oil. The Dirty Motor Oil (DMO) removal test is carried out in the following general manner. Fabric swatches (polyester or polyester/cotton) are laundered in an aqueous bath containing detersive levels (*ca.* 200 ppm) of the chosen anionic/nonionic mixed surfactant system in combination with a "typical" builder-electrolyte mix (600 ppm sodium tripolyphosphate, 250 ppm sodium sulfate, 70 ppm sodium silicate) and a cellulose ether, at varying concentrations. Following the laundering/soil release ether treatment, the swatches are spotted with known amounts of dirty motor oil and relaundered in a commercial, phosphate built detergent (0.12% in the bath) and the soil release ether (12 ppm in the bath); alternatively, the swatches are re-laundered in the mixed surfactants. Soil release can be determined visually, but is preferably compared gravimetrically with control swatches (no soil release polymer treatment).

The DMO test carried out in the presence of surfactant, builder and electrolyte is representative of in-use home laundry conditions involving fabrics heavily soiled with greasy stains. The DMO test indicates that the compositions comprising the herein-specified nonionic-anionic mixtures and cellulose ethers impart substantially better soil release finishes to fabrics than do similar compositions without the nonionic surfactant.

The following examples are typical of the detergent compositions of this invention, but are not intended to be limiting thereof. The granular compositions are conveniently prepared by combining all components except the cellulose ether and the nonionic surfactant in an aqueous crutcher slurry and spray-drying the slurry in standard fashion to provide homogeneous granules. The cellulose ether and nonionic surfactant are thereafter added to the granules. The liquid compositions are prepared by mixing the components in a liquid carrier, which is typically water or water-alcohol (e.g., methanol, ethanol, isopropanol) mixtures. Preferred liquid carriers are water and 100:1 to 10:1 (wt.) mixtures of water/ethanol.

The granular compositions herein are typically used at 1 cup to 1.5 cup levels

in a laundry bath of 15—20 gallons (*ca.* 0.12% concentration). The liquid compositions are typically used at 0.25 to 0.5 cup levels. Typical concentrations of surfactant in the laundry bath are *ca.* 200 ppm (U.S., top-loading machine); builder concentration is *ca.* 600—800 ppm; soil release ether concentration is *ca.* 12 ppm—50 ppm. More or less of the compositions can be employed, according to the desires of the user, depending on fabric and soil loads. In general, the compositions are used at a surfactant: fabric weight ratio of 0.005:1 to 0.010:1.

From the foregoing, it is understood that the nonionic/anionic surfactant mixtures herein are formulated to overcome the incompatibility problem resulting from interactions between the cellulose ethers and the anionic surfactants. It will be appreciated that, even though the nonionic substantially overcomes this problem, it is preferred herein to avoid the use of extremely high concentrations of anionic surfactants with extremely low concentrations of cellulose ethers. Accordingly, the compositions herein are preferably formulated to provide a weight ratio of anionic surfactant: cellulose ether in range from 5:1 to 100:1, most preferably 10:1 to 30:1, thereby avoiding "swamping" the nonionic compatibilizing surfactant and interfering with the cellulose ether.

EXAMPLE I

A phosphate-built granular detergent composition is as follows:

Ingredient	% (wt.)
$C_{11.8}$ alkyl benzene sulfonate, sodium salt*	15.0
n-$C_{16}(EO)_6$	5.0
"Methocel" HB 15000**	1.0
Sodium tripolyphosphate	33.0
Sodium silicate (water-soluble)	10.0
Sodium sulfate	25.0
Minors (perfume, optical brighteners, water, etc.)	Balance

*Comprising C_{10}—C_{16} mixed alkyl benzene sulfonates, avg. alkyl chain length 11.8.

**Methyl hydroxybutyl cellulose; DS methyl *ca.* 2; DS hydroxybutyl *ca.* 0.08; 2% solution viscosity 15000 centipoise; available from Dow Chemical.

The composition of Example I is prepared by spray-drying an aqueous crutcher mix containing all ingredients (except the $C_{16}(EO)_6$ and Methocel HB 15000) to form granules. The granules are then sprayed with the $C_{16}(EO)_6$ and the Methocel HB 15000 is added to the composition as a dry admix.

The composition of Example I is used at a concentration of 0.12% (wt.) in an aqueous laundry bath to launder fabrics. The composition provides good overall oily and particulate soil detergency performance and the fabrics are provided with an oily soil release finish (DMO test).

EXAMPLE II

A highly built detergent composition containing enzymes and especially adapted to European laundering conditions is as follows:

Ingredient	% (wt.)
$C_{11.9}$ linear alkyl benzene sulfonate, sodium salt	20.0
Tallowalkyl sulfate sodium salt	5.0
Mixed tallowalcohol $(EO)_{20}$* ethoxylate	5.0
"Methocel" HB 15000	1.0
Sodium tripolyphosphate	65.0
Enzyme**	0.5
Minors (optical bleach, water, perfume, etc.)	Balance

*Tallow-based alcohol ethoxylated to an average 20 ethoxylate and vacuum stripped to remove substantially all shorter ethoxylates and unreacted alcohols.

**Proteolytic enzyme from *Thermoactinomyces Vulgaris* ATCC 15734.

The granular composition of Example II is prepared in the same manner as that of Example I, with the enzyme being added to the spray-dried granules as an admix.

The composition of Example II is used at a concentration of 0.24% (wt.) in a front-loading automatic washer, avg. water temperature 90°C, to launder a mixed

load of finished and unfinished polyester and polyester/cotton fabrics. The fabrics are provided with a uniform soil release finish.

In the composition of Example II, the "Methocel" HB 15000 is replaced by an equivalent amount of methyl cellulose, avg. DS methyl 2.0; methyl hydroxyethyl cellulose, DS methyl 2.0, DS hydroxyethyl 0.2; and methyl ethyl cellulose, DS methyl 1.0, DS ethyl 0.5; respectively, and excellent soil release finishes are secured.

EXAMPLE III

A detergent composition containing a non-phosphorus detergency buider is as follows:

Ingredient	% (wt.)
Tetradecylbenzene sulfonate, sodium salt	10.0
Sulfated tallowalcohol (EO)$_6$	10.0
"Methocel" HB 15000	1.0
Neodol$_{45}$E$_{12}$*	5.0
Nitrilotriacetate, trisodium salt	25.0
Soluble sodium silicate	10.0
Sodium sulfate	35.0
Minors	Balance

*As defined above.

The granular composition of Example III is prepared in the manner of the composition of Example I. Used at a 1-1/2 cup level in a standard, top-loading machine, the composition of Example III provides good detergency performance and imparts a soil release finish to polyester/cotton blend fabrics.

In the composition of Example III, the nitrilotriacetate is replaced by an equivalent amount of a builder comprising hydrated zeolite A particles (*ca.* 1 micron diameter) and equivalent results are secured.

In the composition of Example III, the nitrilotriacetate builder is replaced by an equivalent amount of a builder consisting of 15:1 (wt.) mixture of sodium carbonate and calcium carbonate particles (particle size avg. 1.0 microns) and equivalent results are secured.

EXAMPLE IV

A liquid detergent composition containing the cellulose soil-release ethers is as follows:

Ingredient	% (wt.)
$C_{11.8}$ alkyl benzene sulfonate, triethanolammonium salt	10.0
"Methocel" HB 15000	0.5
Stripped C_{16}(EO)$_6$	10.0
Triethanolamine	3.0
Ethyl alcohol	10.0
Water	Balance

The composition of Example IV is prepared by blending the ingredients. The composition is used at the 1/4-cup level in a standard top-loading washing machine and provides good detergency performance while concurrently imparting a soil release finish to polyester and polyester/cotton durable press fabrics.

WHAT WE CLAIM IS:—

1. A detergent composition comprising:

(a) from 5% to 65% by weight of a mixed surfactant component comprising a water-soluble anionic surfactant which is an alkyl sulfate, alkyl ether sulfate, alkyl sulfonate, alkyl ether sulfonate or alkyl benzene sulfonate, or a mixture thereof, wherein the term alkyl includes alkenyl groups, said alkyl groups having 8 to 22 carbon atoms, and a water-soluble nonionic surfactant, or a mixture thereof, selected from the group consisting of primary C_8 to C_{20} alcohol ethoxylates containing 9 to 30 ethoxyl groups, secondary C_3 to C_{20} alcohol ethoxylates containing 9 to 30 ethoxyl groups, and C_6 to C_{12} alkyl) phenol ethoxylates containing 9 to 30 ethoxyl groups, said nonionic surfactant being characterized by an EO:hydrocarbon ratio of from 0.6:1 to 3:1, at a weight ratio of anionic surfactant:nonionic surfactant of from 15:1 to 1:1; (b) from 0.1% to 3% by weight of a soil release ether component selected

from the group consisting of alkyl cellulose ethers, hydroxyalkyl cellulose ethers and hydroxyalkyl alkyl cellulose ethers; (c) from 0% to 70% by weight of a detergency builder component; and (d) the balance of the composition comprising detergency adjunct materials and carriers.

2. A composition according to claim 1, characterized by a weight ratio of anionic surfactant: soil release ether component in the range of from 5:1 to 100:1.

3. A composition according to Claim 1 or 2 wherein the anionic surfactant is selected from the group consisting of C_{10}—C_{18} alkyl benzene sulfates, C_{10}—C_{18} alkyl benzene sulfonates, C_{10}—C_{18} alkyl sulfates, C_{10}—C_{18} alkyl sulfonates, ethoxylated C_{10}—C_{18} alkyl ether sulfates and ethoxylated C_{10}—C_{18} alkyl ether sulfonates, or mixtures thereof.

4. A composition according to Claim 3 wherein the anionic surfactant is selected from the group consisting of the alkali metal, ammonium and alkanolammonium salts of C_{10}—C_{18} linear alkyl benzene sulfonates, and mixtures thereof.

5. A composition according to Claim 3, wherein the anionic surfactant is selected from the group consisting of the alkali metal, ammonium, and alkanolammonium salts of C_{10}—C_{18} alkyl sulfates, and mixtures thereof.

6. A composition according to Claim 3 wherein the anionic surfactant is selected from the group consisting of the alkali metal, ammonium and alkanolammonium salts of ethoxylated C_{10}—C_{18} alkyl ether sulfates, and mixtures thereof.

7. A composition according to any one of Claims 1—6 wherein the soil release ether component is selected from the group consisting of methyl, ethyl, propyl and butyl cellulose ethers.

8. A composition according to Claim 7 comprising a methyl cellulose ether characterized by a DS methyl in the range from 1.0 to 3.0.

9. A composition according to Claim 8 wherein the DS methyl is from 1.8 to 2.2.

10. A composition according to any one of Claims 1—6 wherein the soil release ether component is selected from the group consisting of hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl cellulose ethers.

11. A composition according to any one of Claims 1—6 wherein the hydroxyalkyl substituent in the hydroxyalkyl alkyl cellulose ether is independently selected from hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl, and wherein the alkyl substituent is independently selected from methyl, ethyl, propyl and butyl.

12. A composition according to Claim 11 wherein the hydroxyalkyl alkyl cellulose ether is a methyl hydroxybutyl cellulose characterized by a DS methyl in the range of from 1.7 to 2.7 and a DS hydroxybutyl in the range of from 0.01 to 1.0.

13. A composition according to Claim 12 wherein the DS methyl of the cellulose ether is from 1.8 to 2.2.

14. A composition according to Claim 13 wherein the DS hydroxybutyl of the cellulose ether is from 0.06 to 1.0.

15. A granular detergent composition according to any one of the preceding Claims comprising from 15% to 65% by weight of a water-soluble detergency builder.

16. A composition according to Claim 15 wherein the builder is an inorganic detergency builder.

17. A composition according to Claim 16 wherein the inorganic builder is sodium tripolyphosphate.

18. A composition according to any one of Claims 1—15 wherein the builder is a water-soluble organic detergency builder.

19. A composition according to Claim 18 wherein the organic builder is sodium nitrilotriacetate.

20. A composition according to any one of Claims 1—15 comprising from 15% to 65% by weight of a seeded builder.

21. A composition according to Claim 20 wherein the seeded builder comprises a 30:1 to 5:1 weight mixture of sodium carbonate and particulate calcium carbonate having an average particle diameter from 0.01 microns to 5 microns.

22. A composition according to any one of Claims 1—14 comprising from 15% to 65% by weight of a substantially water-insoluble builder which is capable of reducing the hardness content of a laundering liquor.